

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-02-

0296

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1. REPORT DATE (DD-MM-YYYY) 12-08-2002		2. REPORT DATE Final Technical Report		3. DATES COVERED (From - To) April 1999 - March 2002	
4. TITLE AND SUBTITLE Molecular Beam Studies of Reactions Between Stratospheric Gases and Supercooled Sulfuric Acid				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER F49620-99-1-0139	
				5c. PROGRAM ELEMENT NUMBER 61102f	
				5d. PROJECT NUMBER 2303	
6. AUTHOR(S) Nathanson, Gilbert M. (PI) Morris, John R. Behr, Peter M. Splan, Jennifer Glass, Samuel; Torn, Ryan				5e. TASK NUMBER EX	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Board of Regents of the University of Wisconsin System 750 University Ave. Madison, WI 53706-1490				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 N Randolph St. Room 732 Arlington, VA 22203-1977					
12. DISTRIBUTION AVAILABILITY STATEMENT Approve for Public Release; Distribution unlimited					
13. SUPPLEMENTARY NOTES Dr. Michael R. Berman, Program Director					
14. ABSTRACT Sulfuric acid aerosols in the stratosphere contribute to the destruction of the ozone layer by converting inactive gases like HCl and HBr into molecules that fall apart into chlorine and bromine atoms, which catalytically destroy ozone. The first step in these reactions is the transport of gaseous HCl and HBr into the acid droplet, where they dissolve and dissociate. We find that the entry of HCl and HBr into sulfuric acid is often frustrated by immediate HCl and HBr evaporation from the surface of the acid. For mid-latitude, 70 wt % sulfuric acid, only 11% of the HCl and 22% of the HBr molecules that strike the acid surface enter into the bulk. These entry probabilities rise to 70% for HCl and 90% for HBr in 54 wt % sulfuric acid, typical of higher latitudes. We also find that HCl is 20 times more soluble than predicted in 70 wt % sulfuric acid. This high solubility implies that, although few HCl molecules enter mid-latitude aerosols, those that do enter the acid dissolve for longer than expected, making them more likely to react with other solute species.					
15. SUBJECT TERMS Stratospheric Ozone Depletion Gas-Liquid Reactions					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 9	19a. NAME OF RESPONSIBLE PERSON Gilbert M. Nathanson
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code) 608-262-8098

20021015 059

Final Technical Report for AFOSR Grant F49620-99-1-0139

Gilbert M. Nathanson (PI), Department of Chemistry, University of Wisconsin-Madison

AFOSR Grant/Contract Information

Title: "Molecular Beam Studies of Reactions between Stratospheric Gases and Supercooled Sulfuric Acid"

Number: F49620-99-1-0139

Dates: April 01, 1999 - March 31, 2002

Program Director

Dr. Michael R. Berman

AFOSR/NL

801 N. Randolph St., Rm. 73

Arlington VA 22203-1977

Phone (703) 696-7781, FAX (703) 696-8449

Objectives and Accomplishments

This technical report summarizes our studies of reactions of protic gases with supercooled sulfuric acid at concentrations typical of stratospheric aerosols.

Heterogeneous reactions of gas phase molecules with aqueous sulfuric acid aerosols play a significant role in the destruction of ozone in the stratosphere. These processes include the acid-catalyzed reactions of HCl and HBr with ClONO_2 (BrONO_2) and HOCl (HOBr) to generate photoactive halogen molecules, particularly in colder regions of the stratosphere where they are more soluble in the water-rich aerosols. Additionally, the absorption of HNO_3 into the supercooled acid removes nitrogen oxides from the stratosphere and can alter the freezing, growth, and catalytic properties of the aerosols. Our objective is to determine the mechanisms and rate-limiting steps of reactions of these atmospheric gases with these supercooled sulfuric acid droplets. By employing molecular beam scattering techniques, we probe the nature of the initial gas-sulfuric acid collision and the immediate fate of HCl, HBr, and HNO_3 molecules trapped at the acid's surface as they either desorb into the gas phase or react in the interfacial or bulk regions of the aerosol.

During this second grant period, we have used molecular beam scattering of HCl and HBr from 54 to 70 wt % D_2SO_4 at 213 K to investigate the mechanisms of trapping, solvation, reaction, and desorption of these gases in contact with sulfuric acid. These concentrations are typical of sulfuric acid aerosols in the high and mid-latitude stratosphere. We find that halogen-containing molecules HCl and HBr, upon adsorption on the surface of sulfuric acid, will more readily desorb than dissolve and dissociate at acid concentrations above 60 wt % D_2SO_4 for HCl and 63 wt % D_2SO_4 for HBr. This is contrary to the accepted belief that HCl and HBr enter sulfuric acid upon every collision. We have also measured the residence times and solubilities of HCl and HBr dissolved in 54 to 70 wt % sulfuric acid at 213 K. These solubility data are the first measurements at these acid concentrations, and they provide new information strongly suggesting that HCl is much more soluble and more reactive in the mid-latitude stratosphere than originally believed.

New experiments further indicate that the entry of HCl into 65 wt % sulfuric acid increases as the temperature of the acid is raised, perhaps because the surface roughens at higher temperatures, creating more free OH groups that can bind to thermalized HCl molecules. This experimental result contrasts strongly with measurements on more dilute solutions. Finally, we have shown during the last year that short chain alcohols such as butanol segregate to the surface of sulfuric acid but only act as weak barriers to gas transport into the acid.

Specific Accomplishments

- 1) Impinging HX ($X = Cl, Br, NO_3$) molecules transfer their excess energy efficiently to interfacial D_2O and D_2SO_4 molecules and thermalize readily on the surface of 54 to 70 wt % D_2SO_4 at 213 K. Thus, energy dissipation should not limit the number of molecules that enter sulfuric acid aerosols. The trapping probability should therefore be near one for protic gases striking sulfuric acid aerosols in the stratosphere and troposphere.
- 2) The fractions of thermally accommodated HX molecules that undergo H \rightarrow D exchange on 70 wt % D_2SO_4 are $0.10 \pm .03$ (HCl), $0.22 \pm .03$ (HBr), and >0.95 (HNO_3). The small values for

HCl and HBr indicate that only 1 in 9 HCl collisions and 2 in 9 HBr collisions lead to dissolution and dissociation at thermal impact energies; the remaining molecules desorb from the surface before they can enter the acid and dissociate. In contrast, the strongly hydrogen bonding HNO_3 molecule dissolves in nearly every collision. Other hydrogen-bonding gases such as alcohols and carboxylic acids also appear to enter the acid on nearly every collision.

- 3) The H \rightarrow D exchange fractions increase steadily from 0.1 to 0.7 for HCl and 0.2 to 0.9 for HBr as sulfuric acid is diluted from 70 to 54 wt % D_2SO_4 and more D_2O is available for interfacial solvation. The maximum concentrations at which greater than 50% of the HCl and HBr enter the acid rather than desorb from the aerosol surface are 60 and 63 wt % D_2SO_4 , respectively. These results indicate that HCl and HBr do not readily pass through the surface of sulfuric acid aerosols in the mid-latitude stratosphere, where the aerosols are warmer and more concentrated, while they will dissolve more readily in colder and more dilute aerosols found near the polar regions.
- 4) The solvation times for HCl, HBr, and HNO_3 molecules that evaporate before they undergo D \rightarrow H are less than 10^{-6} s, the shortest measurable time in our experiments. This short contact time helps explain why HCl and HBr do not readily dissolve: the contact time is generally too short for solvent D_2O and D_2SO_4 molecules to surround the HCl and HBr molecules before they are propelled from the interface by thermal motions of the surface molecules.
- 5) The residence times for HX molecules that emerge from 70 wt % D_2SO_4 as DX vary from 50 μs for HCl to 2.5 ms for HBr and 0.1 s for HNO_3 . The HBr residence times increase to 30 s as the sulfuric acid is diluted to 54 wt % and stability of solvated Br^- increases. Surprisingly, the residence times for HCl first decrease to a minimum of 10 μs at 65 wt % D_2SO_4 and then *increase* to 300 μs as the acid concentration is raised to 70.5 wt %. There is no parallel turnaround in the H \rightarrow D exchange fractions, which decreases steadily with increasing acid concentration. These results suggest that, after HCl molecules dissolve, they react to form a new species. This species may be ClSO_3D , chlorosulfonic acid, as suggested by Robinson

and coworkers. We could not detect this species in evaporation, indicating that it decomposes into DCl and D_2SO_4 before desorbing.

- 6) HCl and HBr solubilities can be extracted from the bulk residence times reported above. The solubility of HBr decreases steadily with increasing sulfuric acid concentration, in nearly quantitative agreement with independent measurements of HBr solubilities in sulfuric acid. However, the HCl solubilities are 20 to 100 times higher than predicted in 68.5 to 70.5 wt % D_2SO_4 at 213 K. This surprising result indicates that there is 20 to 100 times more HCl dissolved in mid-latitude stratospheric aerosols than previously believed, and therefore that the reaction probability between HCl and HOCl or HOBr may be 20 to 100 times higher than used in present models of the stratospheric reactions.* Tantalizingly, our new solubility data may solve a long standing conundrum in stratospheric field measurements that find there is too little gas phase HCl in the stratosphere (because it is dissolved instead in the acid aerosols). These new implications will hopefully be explored during the next grant period.
- 7) Recent measurements indicate that the $H \rightarrow D$ exchange rate for HCl striking 65 wt % D_2SO_4 increases by 0.12 as the temperature of the acid is raised from 203 to 234 K. Because $H \rightarrow D$ exchange occurs when the HCl enters and dissolves in the acid, this measurement implies that the entry probability increases with acid temperature. We hypothesize that the exchange rate increases (and the HCl desorption rate decreases) because the hotter acid exposes more broken hydrogen bonds at the surface, allowing thermalized HCl molecules more opportunities to protonate interfacial water molecules before they can desorb. To our knowledge, this is the first measurement showing that an entry probability of any gas in any liquid increases with increasing temperature.
- 8) We have begun a new program to determine the effects of organic surfactants on gas transport into sulfuric acid aerosols. This research is motivated by observations that aerosols in the upper troposphere (and perhaps lower stratosphere) contain organic molecules produced industrially and swept up by winds from the ocean. More locally, organic species produced from incomplete burning of jet fuel may also dissolve in sulfuric acid aerosols in

the wake of jet aircraft. These molecules often segregate to the surface of the aqueous aerosols, potentially providing a compact coating that hinders gases from dissolving and reacting in the acid. Surface tension measurements at room temperature and at 213 K show that short-chain alcohols (n-butanol, n-hexanol, n-octanol) each lower the surface tension of 0 to 72 wt % H_2SO_4 solutions. The surface concentrations extracted from the surface tension data via the Gibbs adsorption equation indicate that butanol occupies 40% maximum monolayer coverage at 294 K and nearly a full monolayer at 213 K in 72 wt % H_2SO_4 , while the longer chain octanol readily forms a full monolayer at room temperature.

- 9) We next performed molecular beam scattering experiments from 70 wt % H_2SO_4 solutions doped with butanol and octanol at 213 K. Surprisingly, we find that these surfactants reduce the uptake of ethanol molecules impinging on the acid by less than 20%, even at nearly complete monolayer coverages of butanol and octanol. We tentatively believe that the butanol and octanol surfactants may either be too short to stop H_2O and H_2SO_4 species from mixing with the surfactant layer, or that the monolayers contain significant holes that allow the impinging ethanol molecules to enter into the bulk acid. We are now extending these studies to long chain alcohols, such as hexadecanol, where we expect that these surfactants will form tighter and thicker films that act as substantial barriers to gas uptake. These monolayers may therefore reduce the entry probability of HCl and HBr to values lower than 1%, making gas entry into acidic aerosols the rate limiting step in reactions with HOCl and HBr that produce photoactive halogen molecules.*

*The probability γ for reaction between $\text{HX}(\text{gas})$ and $\text{HOY}(\text{soln})$ in the aerosol is given by $1/\gamma = 1/\alpha_{\text{HX}} + 1/\Gamma_{\text{bulk}}$, where $\alpha \approx \text{H} \rightarrow \text{D}$ exchange fraction is the probability for HX entering the aerosol and Γ_{bulk} is proportional to the reaction rate, $k_{\text{bulk}}[\text{HX}][\text{HOY}]$, inside the aerosol. For the low concentrations of HX and HOY in the stratosphere, Γ_{bulk} is typically much smaller than α_{HX} and therefore limits the reaction probability unless α_{HX} falls below ~ 0.01 . Because Γ_{bulk} is proportional to the solubility of HX , a 20 fold increase in HCl solubility in 70 wt % sulfuric acid increases the overall reaction probability by nearly 20. Surfactant-coated aerosols may reduce α_{HX} to values well below 0.01, making α_{HCl} and HCl entry the rate limiting step in reaction.

Personnel Supported by AFSOR During the Grant Period

Principal Investigator

Gilbert M. Nathanson
Department of Chemistry
University of Wisconsin-Madison
1101 University Avenue
Madison, WI 53706
(608)262-8098 FAX (608)262-9918 nathanson@chem.wisc.edu

The PI is directly supported by AFOSR for one month each year during the summer.

Graduate Students

Jennifer Splan Lawrence will begin her fifth year in September, 2002. She has been supported full time by AFOSR since September, 2000 and partly by AFSOR and by a teaching assistantship since September, 1998. Jennifer's research focuses on the role of organic surfactants in controlling gas uptake into supercooled sulfuric acid. She initially aided post-doctoral scientists John Morris and Peter Behr in their research on the entry and dissolution of HCl and HBr in sulfuric acid.

Samuel Glass will begin his fourth year graduate school in September, 2002. He has been supported full time by AFOSR since September, 2001 and partly by AFOSR and by a teaching assistantship since September, 1999. Sam studies how the entry probability of halogen acids (HCl, HBr, HF, HOCl, HOBr) into sulfuric acid is controlled by the temperature of the acid. He is now aiding Jennifer Lawrence in her studies of surfactant barriers on sulfuric acid.

Undergraduate Students

Ryan Torn, B.S. Atmospheric and Oceanic Chemistry, graduated in May, 2002. He will enter graduate school in Atmospheric Sciences in September at the University of Washington. Ryan was the recipient of the Hilldale and Bookstore Awards for his research with me. He measured the surface tension and surface segregation of short-chain alcohols in sulfuric acid, which will appear in *J. Phys. Chem. B* in August.

Post-Doctoral Fellows

1) Dr. John R. Morris, December, 1996 through July, 1999. John is now assistant professor in the chemistry department at Virginia Polytechnic and State University, in Blacksburg, VA.

2) Dr. Peter M. Behr, July, 1998 through February, 2000. Peter is a senior scientist within the group of Dr. Reinhard Zellner at the University of Essen in Germany.

Together, John and Peter led our group in investigating the reactions of HCl, HBr, and HNO₃ with supercooled, sulfuric acid.

Publications during this Grant Period

Molecular Beam Scattering of Atmospheric Gases from Supercooled Sulfuric Acid:

Collisions of HCl, HBr, and HNO₃ with 70 wt % D₂SO₄, John R. Morris, Peter M. Behr, Melissa D. Antman, Bradley R. Ringeisen, Jennifer Splan, and Gilbert M. Nathanson, *Journal of Physical Chemistry A*, 104, 6738 (2000).

This extensive manuscript describes our proton exchange and residence time measurements of HCl, HBr, and HNO₃ interactions with one concentration of sulfuric acid. The paper introduces new theoretical and experimental techniques for analyzing time-of-flight spectra and describes the first measurements of microsecond residence times of molecules dissolving in liquids. It provides a cornerstone for our future publications.

Reaction and Desorption of HCl and HBr Following Collisions with Supercooled Sulfuric Acid, Peter Behr, John R. Morris, Melissa D. Antman, Bradley R. Ringeisen,

Jennifer Splan, and Gilbert M. Nathanson, *Geophysical Research Letters*, **28**, 1961 (2001).

This communication introduces our central experimental result that gaseous HCl and HBr react with sulfuric acid at rates that depend strongly on acid concentration over a range of acidities typical of stratospheric aerosols. We monitor the competition between immediate desorption and H→D exchange after HCl and HBr thermalize upon collision with the surface of

deuterated sulfuric acid: the exchange probabilities decrease from 0.7 to 0.1 (HCl) and 0.9 to 0.2 (HBr) as the acid concentration is increased from 54 to 70 wt % D_2SO_4 at 213 K. These measurements imply that HCl and HBr desorb faster than they dissociate at higher acidities, impeding the formation of Cl^- and Br^- in more acidic aerosols. However, HCl molecules that do dissolve in 65 to 70 wt % D_2SO_4 are more soluble than expected, increasing their lifetime in solution and potentially their reactivity with other solute species.

Surface Tension and Surface Segregation of n-Butanol in Sulfuric Acid, Ryan D. Torn and Gilbert M. Nathanson, *Journal of Physical Chemistry B*, **106**, August issue (2002).

This paper describes the first measurements of the surface activity of organic molecules in aqueous sulfuric acid. We show that short-chain, soluble alcohols readily segregate to the surface of aqueous acid. This segregation, however, diminishes as the acid becomes more concentrated and the alcohols become protonated and more soluble. At bulk concentrations of 0.2 to 0.4 M butanol, the surface coverage drops from 70% for pure water to 40% for 72 wt % sulfuric acid. The butanol surface coverage rises as the acid is cooled, and approaches 80% or more at 208 K, representative of acid aerosols in the mid-latitude stratosphere. Longer chain alcohols also enhance segregation, suggesting that insoluble molecules such as hexadecanol may efficiently pack at the surface of the acid, providing a barrier to gas transport.

Energy Accommodation in Hyperthermal Gas-Surface Collisions: Relevance to Aerobraking in Planetary Atmospheres, Timothy K. Minton, Masahito Tagawa, and Gilbert M. Nathanson, submitted to the *Journal of Spacecraft and Rockets*, August, 2002. I aided the first two authors in analyzing molecular beam scattering data to determine how efficiently collisions transfer energy from atmospheric gases to spacecraft as they enter into an orbit around a planet, potentially causing the spacecraft to overheat. This work was not carried out under the auspices of AFOSR, but it illustrates the ways in which scattering experiments can help resolve practical issues such as the use of passive braking of orbiting spacecraft.